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# LOGWOOD

# AND ITS USE IN WOOL-DYEING.

BY

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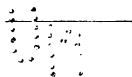
(Result of students' work in Professor Hummel's Dyeing
Laboratory, Yorkshire College, Leeds.)

# INTRODUCTORY REMARKS.

THE following notes, originally contributed to an English trade journal, include many novel observations which are the result of experiments made by students in the Dyeing Department of the Yorkshire College, Leeds; and for permission to make use of these, I am indebted to Professor Hummel.

The views herein expressed with regard to the rationale and utility of the "ageing" process in certain cases were developed in the following manner: — In 1886 Professor Hummel noticed that the dyeing properties of pure hæmatoxylin and hæmateïn differed materially from each other, and with the object of throwing some light upon the real nature of the "ageing" of logwood, dyeing experiments were at once instituted with numerous samples of logwood, both in their "fresh" and "aged" conditions, supplied by various dyewood-cutters. The immediate object was to determine if the dyeing properties of fresh and aged wood corresponded respectively to those of hæmatoxylin and hæmateïn, and also if the "ageing" process caused any real increase in dyeing power.

The results of these experiments were first communicated by Prof. Hummel to the local Priestly Club (Leeds) in 1887; and subsequently appeared, together with the results of additional and confirmatory experiments instituted by the author, in the *Dyer and Calico Printer*, Vol. XI., pp. 7, 8 and 74. They are, however, here published for the first time in separate form.

The publication of this pamphlet at the present time is due to the initiative of Wm. J. Matheson & Co., Ltd. (Drysalters, etc., of New York, Boston, Philadelphia and Providence, U. S. A.), who with sagacity and enterprise have in the same way already issued *several* works for gratuitous distribution to those engaged in the dyeing industry. The fact that Messrs. Matheson find it commercially possible to undertake work of this character, illustrates in a notable way how fast and how far we have travelled during the last 20 or even 10 years, although the old idea of keeping things secret dies hard. The dissemination of useful information in this way is certainly of immense benefit to the trade at large, and will, it is hoped, in the long run amply recompense the distributors.

WALTER M. GARDNER.

YORKSHIRE COLLEGE, LEEDS, June, 1892.

# LOGWOOD.

## ORIGIN AND PRELIMINARY TREATMENT.

This, the most important of all the natural dyewoods, has been in use since the discovery of America. Being the product of a tree growing in the warmer regions of Central and South America, it was for a long time shipped principally from the Bay of Campeachy, and known under the name of "Campeachy wood." The botanical name of the tree, *Hæmatoxylon Campeechianum*, also indicates its connection with that district; but the bulk of the vast quantity used is now imported from Jamaica and Honduras. In appearance the tree somewhat resembles the hawthorn, but it is considerably more massive.

The wood is shipped to this country (England) in the form of logs, with the outer bark removed; but before being used by the dyer, it is, of course, reduced to small chips or to powder, these being called, respectively, "chipped" and "rasped," or "ground" wood. Extracts of logwood are also made and largely used, the ground wood being boiled with water under pressure, and the solution concentrated in vacuum pans. The preparation and properties of these extracts will be more fully dealt with at a later stage.

When first cut down, the wood is light yellowish-brown in appearance, but during storage and transport the color gradually darkens and becomes brownish-red.

## COLORING PRINCIPLES AND COLORING MATTERS.

This change of color is explained by the fact that the coloring principle existing in the growing or freshly cut wood is an almost colorless substance. It has usually been considered

that this substance is, for the most part, a glucoside, which is subsequently decomposed, by a special process, into hæmatoxylin (the true coloring principle) and glucose. In the absence of any experimental proof of the truth of this statement having been given, the experiments here related tend to show that it is more rational to regard the coloring principle as existing in the fresh wood essentially as hæmatoxylin itself.

Hæmatoxylin, of which fresh logwood contains as much as 8 to 10 per cent., was first obtained in a pure state by Chevreul. It may be obtained by extracting freshly ground logwood with water containing a little sulphurous acid, and crystallizing the solution thus produced. A better process, however, is to extract the dry fresh wood with ether, evaporate the ethereal solution, add a little water, and allow to crystallize. It forms colorless or amber-yellow crystals, and, if oxidizing influences be excluded, has practically no dyeing power. By the action of oxidizing agents hæmatoxylin is readily changed into hæmateïn.

*Hæmateïn.*—In the case of most of the natural coloring matters it has been found that the substance which is actually of use as a dye does not pre-exist in the living plant, but is only produced during what may be considered as the first stages of decay. In such cases the original substance may conveniently be termed "coloring principle," in contradistinction to the "coloring matter" produced from it, which is alone of practical use. Thus logwood contains the coloring principle hæmatoxylin, which in turn yields the coloring matter hæmateïn.

Hæmateïn is a brownish-red substance, practically insoluble in cold water, but dissolving to a slight extent in hot water. It is more soluble in alcohol. When crystalline, it possesses a somewhat greenish-gray metallic lustre, but it is not easy to obtain it in a crystalline form in any considerable quantity. The green bronzy appearance often noticed on logwood chips is not, however, due to hæmateïn, but to the presence of its ammonia or other alkali compound.

Hæmatoxylin has a great affinity for oxygen, especially in the presence of an alkali, and although hæmateïn is the first substance produced, it is not the final one, hæmateïn itself being readily changed into brown substances by further oxidation. This important fact, that hæmatoxylin, which has no

dyeing power in itself, is readily changed by the action of oxidizing agents into the useful hæmateïn, and that this, again, is very easily destroyed by continued oxidation, should be carefully kept in mind; because upon this one fact are based several processes of very great practical importance.

The following notes of experiments upon the dyeing properties of pure hæmatoxylin and hæmateïn * served as a basis for many experiments bearing upon the "ageing" process.

*Experiments with Hæmatoxylin.*—When wool is mordanted with bichromate of potash and tartaric acid, in which case the fibre is green, the addition of calcium acetate or carbonate to the hæmatoxylin dye-bath is very beneficial; indeed, it is all-important. About 0.5 per cent. hæmatoxylin without any addition in the dye-bath gives a very pale indigo-blue shade, whereas with the addition of 2 to 40 per cent. calcium acetate, the coloring power is greatly intensified, a deep indigo-blue being ultimately obtained. The addition of calcium carbonate to the dye-bath is not so beneficial as the acetate. When the wool is mordanted with bichromate of potash alone, in which case the mordanted wool is yellow, the addition of calcium acetate—even in such small amount as 2 per cent.—is injurious, while with 40 per cent. only a dull greenish-gray is obtained. The greenish tint is probably caused by the formation of chromate of lime. Calcium carbonate in this case is not so injurious as the acetate. When the best colors obtained with the two mordants are compared with each other, it is at once evident that the green mordanted wool, with the use of lime salts in the dye-bath, gives a much brighter and purer color than does the yellow mordanted wool without the use of lime salts, although in the latter case the color has a darker appearance.

*Experiments with Hæmateïn* —When wool is mordanted with bichromate of potash and tartaric acid, the addition of $\frac{2}{3}$ per cent. of calcium acetate or chalk to the hæmateïn dye-bath is beneficial, but only in a comparatively small degree, the indigo-blue color being thereby rendered slightly darker. With the addition of larger amounts of lime-salt the color becomes paler, particularly in the case of chalk. When the wool is

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* See Hummel, Jour. Soc. Dy. and Col., 1886, pp. 79, 80.

mordanted with bichromate of potash alone, hæmateïn yields dull grayish-blue colors, either with or without the addition of lime-salts. It is remarkable that none of the hæmateïn colors obtained on the yellow mordanted wool are at all comparable in depth or brilliancy with those obtained on the green mordanted wool. Dyed with 0.5 per cent of hæmateïn, the green mordanted wool yields a full, rich indigo-blue color, while the yellow mordanted wool gives a comparatively dull-bluish slate.

The general result of these experiments is that the addition of calcium acetate or chalk is much more necessary in the case of hæmatoxylin, the lower oxidized coloring principle, than in the case of hæmateïn, the more highly oxidized principle. This result may lead one to infer that with hæmatoxylin the lime-salt is necessary, in order to facilitate the oxidation of hæmatoxylin into hæmateïn. This view seems also to be supported by the fact that, when bichromate of potash is used alone as a mordant, the addition of lime-salt to the hæmatoxylin dye-bath is not necessary, since the oxidation of the hæmatoxylin then takes place in the dye-bath by reason of the bichromate of potash contained in the mordanted wool. The addition of lime-salts in this case indeed is injurious, just as it is when hæmateïn is employed, since then it may tend to oxidize still further and thus destroy the hæmateïn. Another conclusion seems to be that, if bichromate of potash alone is the mordant used, it is positively injurious to have the coloring matter in the more fully oxidized form of hæmateïn. In other words, when hæmateïn is the coloring matter employed, green mordanted wool must be used in order to obtain the fullest and brightest color. Finally, if green mordanted wool is employed, the advantage of having the coloring matter in the form of hæmateïn rather than of hæmatoxylin is, that a smaller amount of lime-salt is requisite to be added to the dye-bath.

### THE "AGEING" OF LOGWOOD.

This process, which is also called the "curing," "maturing" or "getting-up" of the logwood, has for its object the production of the maximum amount of hæmateïn.

The "ageing" process is usually conducted as follows: The ground or chipped wood is spread out upon a wooden

floor in layers about 12 inches in thickness, a certain amount
of water (30-40 per cent. of the weight of logwood) being
added. Several such layers having been placed on each other,
the whole is well mixed together by means of wooden spades.
Another method is to mix successive quantities of the wood
with the requisite amount of water in a large wooden drum or
dash-wheel, which is then revolved until the whole of the water
is thoroughly absorbed by the wood. The wet wood is then
spread out on floors as before. After standing for some time
a slight heating of the mass ensues, and the color becomes
gradually darker. The operation lasts altogether for several
weeks, the time varying according to the temperature of the
air, being shorter in summer than in the winter months. Dur-
ing the whole operation the wood is several times turned over
and remixed, in order to insure, as far as possible, an equality
of result. The time for remixing is determined by the tem-
perature of the middle of the heap of wood, and this is judged
by withdrawing a wooden rod inserted for the purpose, and
grasping it with the hand. A thermometer affixed to the rod
would give greater precision. If the process is allowed to
proceed too far, the wood gradually loses its rich brownish-
red color, becoming dark yellowish-brown in appearance. It
is then technically known as " burnt " or " overaged " wood,
and its value as a dyestuff is materially lessened, if not de-
stroyed. Great care and constant attention are therefore
necessary during the " ageing " process.

Now with regard to the chemistry of the process. It may
be stated in the first place that the experiments already re-
ferred to showed that in dyeing properties freshly cut log-
wood acts in an exactly similar manner to hæmatoxylin, and
properly aged wood to hæmateïn; further, that the dyeing
power of the wood was not increased. It appears probable,
therefore, that the only essential change occurring in the wood
during the " ageing " process is an oxidation of the former
into the latter, although other of the extractive matters exist-
ing in the fresh wood will also doubtless be modified. Owing
to the presence of nitrogenous matters, the slight fermentation
which takes place as an accompaniment of the process causes
the evolution of a small amount of ammonia which will assist
the oxidation, because hæmatoxylin is much more sensitive to

this influence in the presence of alkalis. If the oxidation is allowed to proceed too far, of course, the hæmateïn is destroyed.

It is evident that this view, that "ageing" consists essentially of an oxidation, is becoming more and more recognized, since, within the last year or two, patents have been taken out for more expeditious processes of "ageing," in which chlorine and compressed oxygen respectively are the active agents— both, of course, acting simply as oxidizers. They would have no effect if the ageing process consisted in decomposing a glucoside.

If the view that the "ageing" process is merely one of oxidation be correct—and it admits of little doubt—then the general opinion that "ageing" is an essential preliminary to the use of the wood in dyeing certainly needs modification. In cases where the mordant employed exerts an oxidizing action, it will probably be found most advantageous to use the coloring matter in the unoxidized, or, at any rate, only partially oxidized state, the necessary change being then completed by the mordant in the dye-bath. If already fully oxidized wood is used, there is undoubtedly in all such cases of dyeing a destruction of a portion of the hæmateïn through overoxidation by the mordant. The rapidly increasing use of extract of logwood, which consists for the most part of unoxidized coloring matter, shows at once that for many purposes the ageing process is not regarded, even by dyers, as essential.

We append patterns of woolen cloth dyed with "fresh" and "aged" logwood (from the same lot of wood), after mordanting with two oxidizing mordants (bichromate of potash; chromic acid) and one non-oxidizing mordant (bichromate of potash reduced by tartaric acid). It will be seen that in the former cases the "fresh" wood (Patterns 1 and 3) gives distinctly better and brighter shades than the "aged" wood (Patterns 2 and 4), the reason being that with the latter a part of the hæmateïn is oxidized and destroyed. With the last-mentioned (non-oxidizing) mordant the "aged" wood has given the best result (compare Patterns 5 and 6), although, as will be seen hereafter, even in this case the process can be so modified that the "fresh" wood can be used, by causing the oxidation of the hæmatoxylin to take place as before in

the dye-bath. A pattern (No. 7) is also given which shows the effect of dyeing with "overaged" wood. The haematein is here destroyed to a considerable extent, and the shade, of course, is very poor.

When using an oxidizing mordant, with any considerable amount of "fresh" wood, it is probable that the amount of mordant fixed on the wool in the mordant-bath will possess insufficient oxidizing power to entirely change the haematoxylin into haematein in the dye-bath. In such cases, therefore, we must either use a partially oxidized ("aged") wood, or add some substance to the dye-bath to assist the oxidation. The latter course is much to be preferred, since the whole process of oxidation is then under the control of the dyer.

From a consideration of the above facts we arrive at the important conclusion that the ageing of logwood may for many purposes be entirely dispensed with, *e. g.*, in dyeing blues and blue-blacks. It may be regarded as a survival from the time when logwood blacks were dyed upon the iron mordant (a non oxidizer); but since bichromate of potash (an oxidizer) is now almost universally employed, the *raison d'être* of the ageing process has to a great extent disappeared; and, if in the near future it is not entirely dispensed with, it ought, at any rate for many purposes, to be materially curtailed.

The results of the confirmatory experiments bearing upon the subject and already alluded to, are detailed below. As mentioned previously, the use of compressed oxygen and chlorine respectively has been patented for the purpose of expediting the ageing process. In the former case it is proposed to place the freshly ground and damped wood into a closed iron vessel placed horizontally and capable of being rotated ; compressed oxygen is admitted by means of a perforated pipe entering at the axis, and it is stated that the change from haematoxylin into haematein is completed in a few hours instead of as many weeks. The action is also more regular on account of the agitation of the wood being constant, instead of very intermittent as in the ordinary maturing process. This process was repeated on an experimental scale, but instead of using freshly ground wood, an extract was obtained from it by heating with distilled water, from which the air had previously been removed by boiling. A portion of this extract was reserved for dyeing, and into the

remainder, inclosed in a long vertical glass tube, compressed oxygen was slowly passed for four hours. A comparative dyeing trial made with equal volumes of the two solutions upon a non-oxidizing mordant showed clearly that the change from hæmatoxylin · into hæmateïn (*i. e.*, the "ageing ") had been at any rate partially effected.

In the next series of experiments an endeavor was made to age the wood by moistening it with dilute solutions of bleach-ing-powder, and allowing the mixture to stand for several hours. In all cases the results of the experiments were judged by comparative dyeing trials, using a mordant which could not affect the results; and it was found that a sample of wood which had been moistened with bleaching-powder solution gave a darker shade than one wetted simply with water. Since, however, the calcium of the bleaching-powder will tend to form a compound with the coloring matter, it might be argued that the difference in color of the dyed samples was due to the production of this compound, and not to the change of hæmatoxylin into hæmateïn.

In order to avoid this complication, the use of some oxidizing agent, free from this defect, is required; and peroxide of hydrogen at once suggested itself as being eminently suitable for the purpose, since it might fairly be considered that any action it exerted would be purely one of oxidation. On re-peating the experiment mentioned above, with hydrogen peroxide in place of bleaching-powder, it was found that the former was, indeed, much more effective; the change from hæmatoxylin to hæmateïn, and the overoxidation of the latter, being distinctly marked. By regulating the amount of $H_2O_2$ employed, one may thus produce a partially oxidized, fully oxidized, or overoxidized wood at will. The ageing process, which usually occupies several weeks, may, therefore, be brought about in a few hours (or even less) by mixing the fresh logwood with the necessary amount of hydrogen peroxide, although probably the expense of the latter will prevent its practical adoption for this purpose.

Having found that $H_2O_2$ effected the necessary change so readily by a treatment of the wood *previous* to the dyeing operation, it seemed desirable to try the effect of adding the peroxide to the dye-bath, using "fresh" wood, *i. e.*, wood

which had not undergone any preliminary treatment. The result was very striking, the shade obtained being even better than those produced by the wood treated previously with $H_2O_2$. The experiment was carried out as follows: Six pieces of woolen cloth, numbered 1 to 6, and each weighing 10 grams, were mordanted for one and a half hours in a solu· tion containing 3 per cent. bichromate of potash and 10 per cent. tartaric acid in one litre distilled water, at the boil. The large amount of tartaric acid was used in order to insure the complete reduction of the $K_2Cr_2O_7$ ; and the mordanted cloth, of course, presented a green appearance. The dyeing was then conducted in the following manner :

1. 15 per cent. dry freshly cut logwood.
2.    "      "      "      + 1cc. $H_2O_2$ (12 vols.)*
3.    "      "      "      + 2cc.    "
4.    "      "      "      + 5cc.    "
5.    "      "      "      + 10cc.  "
6.    "      "      "      + 20cc.  "

In each case one litre of distilled water was used, and the dyeing continued for one and a half hours.

*Result.*—From No. 1 to No. 4 the shade gradually increased in depth. No. 5 was lighter than No. 4, and in No. 6 a gray only was produced. In the two latter patterns the coloring matter was evidently overoxidized (overaged), and a subsequent experiment using amounts of $H_2O_2$, varying from 3cc. to 7cc., showed that (for the particular sample employed) 1.5 gram " fresh " logwood with one litre distilled water require an addition of from 4 to 5cc. $H_2O_2$ (12 vols.) in order to completely change the hæmatoxylin into hæmatein. It has, however, not yet been determined whether this is a constant ratio between $H_2O_2$ and coloring matter, or whether it is influenced by such conditions as concentration of bath, rate at which the temperature of the bath is raised, etc. Of course, samples of wood containing more or less hæmatoxylin than the one used will require a different amount of $H_2O_2$, and the

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* The sample of $H_2O_2$ employed in these experiments was entirely free from barium salts, a common impurity in commercial $H_2O_2$.

We give patterns illustrating these various methods of developing the coloring matter (compare Nos. 5, 6, 8, 3, 9).

It will be noticed that the pattern dyed with wood aged in the usual way is the darkest shade of all. This is, in all probability, due to the fact that the black color obtained when chromed wool is dyed with logwood is really a compound color; consisting of (1) the hæmatein-chromium compound and (2) the chromium compound of the brown oxidation product (overaged wood). This is equivalent to stating that some overoxidized coloring matter is essential to the production of a real black. The same object might, however, be also obtained by ageing the logwood correctly and making suitable small additions of other coloring matters (red and yellow) to the dye-bath.

### LOGWOOD EXTRACTS.

Having discussed the treatment which logwood undergoes when used by the dyer in the chipped or rasped state, the methods used for the preparation of the extracts may now be considered.

The fact that the use of dyewood extracts has largely extended in recent years is capable of easy explanation, since they possess several obvious advantages. Familiarity with the powerful and completely soluble coal-tar coloring matters has made dyers somewhat impatient of the trouble caused by the natural dyestuffs, which, in addition to their bulkiness, leave a large amount of solid residuum (woody matter). Again, it is absolutely necessary in the dyeing of slive·s (tops), curl-cloths, etc., and very desirable when treating loose wool, yarn, etc., in fact in all cases, that the dye-bath should be entirely free from solid particles, since, otherwise, injury to the fabric or waste of material are difficult to avoid. From this point of view, then, soluble extracts are always to be preferred. Another incidental advantage is gained by their use, from the fact that no solid matter need be sent down the drains—a serious consideration in districts where the Rivers Pollution Act is put into force. Again, it is not possible to extract the coloring matter from a dyewood completely during an ordinary dyeing operation; there is always a loss of from 5

to 10 per cent. of coloring matter, while a properly made extract contains, practically, the whole of the coloring matter contained in the original wood. The smaller amount of labor required in handling an extract, which is at most one-tenth the bulk of the wood from which it is produced, has already been referred to.

Against these undoubted advantages must be placed the fact that the extracts are much more open to adulteration than the woods, and, in fact, samples are frequently met with which are very largely reduced in strength by the admixture of foreign matter. In the case of logwood another weak point, which, however, is common to both extracts and "aged" wood, is that the degree to which the coloring matter has been oxidized is very uncertain. The only way to get over this is for the dyer to use "unaged" wood and make his own extracts, unless a standard article can be depended upon. It should be stated, however, that some extract-manufacturers send out products which are excellently made, oxidation being entirely avoided, and which contain no added impurities.

The question arises, then, whether it is more advantageous and economical for dyers to buy a good brand of extract, or to obtain the wood and extract the coloring matter themselves ? Probably a review of the best methods applicable in each case will help us to arrive at a just conclusion.

For the manufacture of logwood extract on a large scale two principal methods are in vogue. These are known as the French and American processes, since they were first worked respectively in those countries. In the French process the extraction of the wood takes place in open pans with warm or boiling water, while in the American system closed vessels are employed, and steam at a pressure of 15 lbs. to 30 lbs. is used for the extraction. In either case the extract is afterwards concentrated by evaporation, and sold as "logwood liquor" at about 15 deg. T. W.; "logwood extract" at about 51 deg. T. W., or in the solid state as "solid logwood extract." The concentration is best conducted in vacuum pans.

Each of these two processes has its strong advocates, since each appears to possess certain advantages. A wood which yields 16 per cent. of extract by the French process, will give

at least 20 per cent. if extracted under pressure; [*] but since this extra 4 per cent. consists largely of extractive substances other than coloring matter, the apparent advantage of the second method is largely discounted. It has been freely stated that extract made at the lower temperature gives brighter shades than that produced under pressure, and it is certainly true that too high a temperature or too long continued extraction will give an inferior product on account of the oxidation of the coloring matter.

The extract is usually made from " unaged " logwood, and this is rational for several reasons. In the first place, hæma·toxylin being much more soluble in water than hæmateïn, the coloring matter is more easily extracted when in the former state; second, during the process of extraction and concentration a certain amount of oxidation is inevitable, and this leads to destruction of coloring matter, if it is already present as hæmateïn; third, as previously shown (see p. 10), the coloring matter can be most usefully employed in the form of hæmatoxylin.

Working under quite erroneous impressions, some makers have oxidized the coloring matter previous to extraction; and such substances as ammonia, chalk, chlorates and nitrates of soda and potash, etc., have been proposed and used for this purpose, with the result that a good deal of extra trouble has been taken to produce a much inferior article.

Although, as already stated, some manufactuiers produce extracts which leave little to be desired in the way of purity, this can hardly be considered as the rule. Admixture with such substances as molasses, glucose, dextrin, tannin extracts, etc., is so easily carried out, and yet so difficult to detect, that it is apparently an irresistible temptation. The fact that many dyers use quite unreliable methods of testing extracts also favors this course. Even the best methods of examination known to chemists are apt to be misleading unless conducted with discretion, since the extractive matters, organic or inorganic, naturally present in different samples of logwood, vary considerably both in amount and character. The proportion of ash in the wood, for instance (mostly soluble in

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[*] Soxklet, Chem. Zeit., No. 41, 1890.

water), may vary from 0.8 to 2 per cent., and the total ex-
tractive matter from 14 to 22 per cent. of the weight of the
wood.* The percentage of ash in the *extracts* may, therefore,
vary very much, indeed, without there being any intentional
adulteration, and depends to a large extent upon the method
of extraction employed. It is even possible, as pointed out by
Bruehl, to reduce the percentage of ash by adulterating the
extracts with such substances as molasses or tannin extracts.
A determination of the ash, therefore, affords no reliable in-
formation with respect to the purity of an extract, although
the presence of chalk or sodium sulphate in any considerable
quantity is sufficient evidence of adulteration. The detection
and estimation of such substances as these, of course, offers no
difficulties.

### EXAMINATION AND VALUATION OF LOGWOOD EXTRACTS.

Since the proportion of coloring matter in different samples
of logwood may vary greatly, even though they yield the
same amount of extract of a given strength, it is evident that
the mere specific gravity of the latter is no measure of its
coloring power.

Thus the use of the hydrometer for the purpose of valuing
extracts is not only useless, but very misleading. Again,
even if it were possible to determine accurately the presence
and amount of adulteration, this would give no indication of
the actual percentage of coloring matter; because an extract
made from a wood rich in hæmatoxylin may be considerably
reduced in strength by adding foreign matter, and still con-
tain a greater percentage of coloring matter than an unadul-
terated extract made from poor wood. The actual amount of
coloring matter present is, therefore, the only true test of
value. Even this, however, is not sufficient. It is not only
necessary to know the total amount of coloring matter pres-
ent, but also to determine in what state of oxidation it exists;
*i. e.*, what proportion of hæmatoxylin and hæmateïn respec-
tively are contained in the sample.

Most of the methods which have been proposed for the

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. * Bruehl, Farb. Zeit., 1887-8.

valuation of logwood extracts do not discriminate between these two substances, and are thus inherently defective. Because if the extract is to be used by a process applicable for (say) hæmateïn, it will inevitably produce poor results if it consists principally of hæmatoxylin, although possibly it may be rich in coloring power. For example, take the case of two samples, one containing 75 per cent. of hæmatoxylin and the other an equivalent amount of hæmateïn. If used for dyeing wool prepared with chromic oxide (*e. g.*, mordanted with chromium fluoride) the latter would appear infinitely the stronger sample of the two in practical work, although the laboratory test might have shown the two samples to be of equal value. If, however, a method of analysis had been employed in which the hæmatoxylin and hæmateïn were separately estimated, the cause of the different dyeing results would be at once apparent, and the practical process could be so modified (in a manner to be discussed at a later stage) that the first sample would give equal or even superior results to the one containing hæmateïn.

It may thus happen, and no doubt often does occur, that a dyer finds what is really a good extract to give a worse result by his usual process than one intrinsically less valuable which happens, however, to be adapted to his process; whereas, if he knew not merely the amount of coloring matter, but also the state of oxidation in which it exists in the good extract, he might so alter his process that the full value could be obtained from it.

A further point which may make an extract not only apparently, but actually of more value than another of precisely equal coloring power, is the character of the impurities or adulteration. For example, an extract to which 20 per cent. tannin extract has been added is much inferior for wool-dyeing to one of the same coloring power reduced with an equal amount of molasses, because tannin matters tend to give the wool a harsh, unpleasant feel, and are thus injurious. For many cotton-dyeing purposes, however, the two will be reversed in value, since the tannin matter combining with the iron used as mordant helps to intensify the black.

We are now in a position to see what information a satis-

factory method of analysis should yield, and may consider
that the following points should be determined :

   1. Amount of hæmatoxylin.

   2. Amount of hæmateïn.

   3. Character and approximate amount of impurities.

At present there seems to be no analytical method in vogue
which satisfactorily determines all these points, although
much discussion prevails concerning certain processes. The
offer of a medal by the Société Industrielle de Rouen for " an
easy and exact method of determining the pure hæmateïn in
logwood extracts," has no doubt acted as an incentive to
chemists in their endeavor to devise such a process; but the
Society would have done well to have insisted upon a deter-
mination of all the three points mentioned above.

The process which it appears desirable to adopt for the
testing of logwood extracts will be fully dealt with in a sepa-
rate pamphlet.

### APPLICATIONS OF LOGWOOD.

A very simple experiment is sufficient to show that logwood
in itself, uncombined with any other substance, has practically
no coloring power. If a piece of wool is boiled in a decoction
of logwood, in distilled water, the wool acquires only a pale-
brown or drab color, which can be almost entirely removed by
washing in a weak soap solution; the wool is not dyed, but
merely stained. If, however, the wool is previously prepared
with a suitable solution of a chromium, iron or other metallic
salt, on boiling with logwood a permanent blue or black color
is produced.

Logwood must be applied in conjunction with some metallic
mordant, and the colors produced upon the wool are definite
chemical compounds formed by the combination of the coloring
matter — hæmateïn — with the metals chromium, iron, copper,
etc., as the case may be. These color-lakes, moreover, vary
somewhat in color, although they are not so strikingly different
as with many other dyestuffs. Confining our attention to the
commonly used mordants, it is from that the chromium-hæma-
teïn compound is blue-black or indigo-blue, the tin lake is pur-
ple, while iron produces a grayish black, alum a purplish black,
and copper a green black. (See Patterns 10, 11, 12, 13, 14.)

### ACTION OF LIGHT UPON LOGWOOD-COLORS.

In addition to being variously colored, these compounds show considerable differences with respect to the way in which they withstand the action of light. The tin and aluminium compounds are the most fugitive, fading somewhat rapidly to grays. The chromium and iron shades are about equal in fastness, and may be considered about twice as fast as the above, but, whereas the iron-color fades to a gray, the chromium changes to a dull green or grayish green; and this, as is well known, is the most objectionable feature of the chromium-logwood blacks. This matter will be more fully discussed at a later stage. The copper-hæmatein lake is considerably more permanent than that obtained with either chromium or iron, being little affected by twelve months' exposure to the light; and, although this fact is already on record, it is not generally known.

The principal use of logwood in dyeing is for the production of blacks, although it is also largely employed in conjunction with other coloring matters for producing grays, browns, drabs, olives, etc.; in fact, it is by far the most generally used of all known dyestuffs.

Logwood is also an extremely cheap coloring matter. If we take it that the wood as sold (containing 33 per cent. moisture) contains 5 per cent. of hæmatein—a very moderate estimate— and that the sample is sold at £6 per ton, the pure coloring matter will cost about a shilling a pound, and will be equal in coloring power to ten times its weight of alizarin blue at (say) one shilling per pound, or to twice its weight of any of the coal-tar blacks at (say) two shillings per pound. In comparing the actual cost of the dyed colors, it is, however, necessary to take into account the cost of the mordants, labor, steam, etc., which being much greater in the case of logwood than of the coal-tar blacks, would thus reduce the cost of a black dyed with the latter almost, and in some instances quite, to that of a logwood-black.

The subject of black dyeing with logwood is so important and extensive that it is well to consider it in some degree of detail. Chromium and iron are the only two metals which are employed as principal mordants, but copper, aluminium

and tin are often used as secondary mordants for the purpose of modifying the shade or the properties of the color. Thus one may distinguish two classes of logwood-blacks : chrome blacks and iron-blacks, the latter being often called copperas-blacks. A third class should also be mentioned, viz., woaded-blacks, which, however, are not simple logwood-colors, but are obtained by first dyeing a medium shade of blue in the indigo vat, then mordanting, and, lastly, dyeing with logwood.

### THE TESTING OF LOGWOOD-BLACKS.

The three classes of blacks may readily be distinguished from each other as follows :

*Chrome-blacks and iron-blacks.*—Upon cloth dyed chrome-black a drop of sulphuric acid at 100 deg. TW. produces an olive-brown spot, while an iron-black gives a crimson-red spot. This test must, however, be applied with care, since too weak acid produces a crimson spot on both, and more concentrated acid gives a brown spot with both iron and chrome blacks. The particular metal used as mordant may also be determined, if considered advisable, by burning a piece of the cloth and examining the ash by means of the usual chemical tests.

*Woaded-blacks and chrome or iron blacks.*—In the case of both chrome and iron blacks a cherry-red solution is obtained if the cloth is boiled in a solution of sulphuric acid at 4 deg. TW. ; and by repeating this operation two or more times the whole of the logwood may be removed. If dyed with log-wood only, the cloth appears of a yellow-brown color. Since indigo-blue is quite unaffected by this acid treatment, the amount of indigo in a woaded-black may be roughly estimated by washing and drying the cloth and examining the amount of color which remains. The color may vary from dull blue to gray, and if spotted with strong nitric acid the yellow stain, which is considered characteristic of indigo-blue, will be produced. The spot, however, as a rule, has a brown tinge, and is not greenish-yellow as with pure indigo-blue.

Vat indigo-blue is one of the most permanent dyes known, while the logwood-colors must take second or third rank in this respect. It is evident, therefore, that a dye consisting of a combination of the two will be faster the more indigo it

contains, and more and more fugitive as the amount of log-wood is increased. But if submitted to the above tests, it will be found that many reputed "woaded-blacks" contain in reality no indigo at all, or so little that it cannot influence the permanence of the color. In such cases the use of the term "woaded-black" is unwarranted and misleading.

The methods used in dyeing the various classes of logwood-blacks may now be discussed, and attention will be drawn to several novel and interesting points.

*Chrome-blacks.*—There are several chromium-salts which are used as mordants for wool, although bichromate of potash is by far the most commonly employed. They may be classified as follows:

1. Compounds derived from chromium trioxide ($CrO_3$), viz.: The bichromates of potassium ($K_2Cr_2O_7$), and sodium ($Na_2Cr_2O_7$).

2. Salts derived from chromic oxide ($Cr_2O_3$), viz.: Chrome alum ($K_2Cr_2(SO_4)_4 24H_2O$), and chromic fluoride ($Cr_2 F_6 4H_2O$).

There is an essential difference in the behavior of these two classes of chromium compounds when used as mordants; and this arises from the fact that in all probability the substance which ultimately combines with the coloring matter, whatever the mordant originally employed, is one in which the chromium is in the state of oxidation, as it is in chromic oxide ($Cr_2O_3$. This is of course obtained in a direct manner from the compounds of the second class, by simple decomposition or dissociation; whereas, whenever the bichromates are employed, a reducing action must be brought into play before obtaining the chromic hydrate, which in the strictest sense of the word may be regarded as the true mordant. A glance at the following equations will help to make this clear, although they must be taken simply as illustrations, and not as representing actual reactions:

First class—

$K_2Cr_2O_7 + 4H_2O = Cr_2(OH)_6 + 2KHO + O_3$. That is, three atoms of oxygen must be removed before chromic hydrate can be obtained.

Second class—

$K_2Cr_2(SO_4)_4 + 6H_2O = Cr_2(OH)_6 + K_2SO_4 + 3H_2SO_4$.

It is evident then that the bichromates when used as mordants must be reduced at the expense of either the wool or the coloring matter, or of some other substance which is specially added to the mordant or dye-bath for that purpose. Moreover, since compounds of $CrO_3$ are yellow or orange-colored, while those of $Cr_2O_3$ are green, it will be obvious why the former (bichromate of potash, etc.) are spoken of as the yellow or oxidizing mordant, and the latter (chrome-alum, etc.) are named the non-oxidizing or green mordant.

Turning now from these general considerations, the methods used in applying the various mordants will be discussed.

### BICHROMATE OF POTASH.

So much has been written upon the subject of the use of this mordant that it would occupy far too much space to enter fully into all the issues raised.

With regard to the process adopted, the almost universal plan is to mordant first and dye afterwards in another bath. As shown below, however, the " one-dip " or " single-bath " method may in some cases be employed with advantage.

The simplest case is that in which the wool is mordanted with bichromate alone, and dyed with logwood without addition. With 3 to 4 per cent. (of the weight of wool) of $K_2Cr_2O_7$, and 30 to 40 per cent. dry logwood, this gives a blue-black shade.

Whenever bichromate of potash and logwood are used in conjunction, it is a matter of great importance that the amount of the mordant should be within certain well-determined limits. If less than 2 per cent. (of the weight of wool) is employed, the shade obtained is poor and dull; while, if 5 or 6 per cent. is much exceeded, the coloring matter (hæmatein) may be partially destroyed.

*Overchroming.*—Wool thus prepared with an excess of bichromate, more particularly when sulphuric acid is used along with it, is said to be "overchromed," and cannot by ordinary methods be dyed black with logwood, whatever amount of the latter is used. The reason of this fact is somewhat obscure. The first action will undoubtedly be that hæmatein is oxidized and destroyed by the excess of bichromate, the latter at the

same time being reduced. If this was the only action, however, it is evident that by continually adding logwood the whole of the bichromate would eventually be reduced, and a black would be obtained by using a further quantity of logwood. That this is not the case proves this explanation to be insufficient.

The following ideas are therefore put forward as perhaps more correctly interpreting the facts, although it is possible that further experiments may lead to their modification.* Special experiments showed that an amount of hæmatein corresponding to the amount of bichrome present was oxidized, but at the same time the oxidation products of the hæmatein combined with the chromium, becoming fixed upon the wool and imparting to it a brown color. The whole of the mordant fixed on the wool being thus in combination with brown coloring matter and thereby saturated, the wool was practically, as regards any further quantity of logwood, in an un-mordanted condition. It was found, however, that if over-chromed wool, after dyeing with excess of logwood to reduce and saturate the mordant, was then re-mordanted with a normal amount of bichromate and re-dyed with logwood, a black could be obtained, although it always appeared somewhat brownish, owing to the fact that the color is a compound dye, consisting of a normal logwood black, together with excess of the brown oxidized-hæmatein dye.

When dyeing chrome-blacks, many modifications may be made, both in mordant-bath and dye-bath.

The bichromate of potash may, with some advantage as regards cost, be substituted by sodium bichromate. The latter is sold as an anhydrous mass ($Na_2Cr_2O_7$) or in crystalline form ($Na_2Cr_2O_7 2H_2O$). The latter having practically the same molecular weight as $K_2Cr_2O_7$, may be used in equal quantity, but a somewhat smaller amount of the anhydrous $Na_2Cr_2O_7$ should be employed, since $\frac{3}{5}$ parts are equivalent to 4 parts $K_2Cr_2O_7$. In whatever form the mordant is used, however, the amount should vary according to

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* The following explanation of the fact that "overchromed" wool will not dye black was first suggested by Mr. T. H. Wheelwright, a student in the Dyeing Department of the Yorkshire College.

the depth of shade required, *i. e.*, according to the percentage of logwood which is to be used in the dye-bath. This is very important, because the degree of fastness against the action of the light of logwood grays and blacks depends to a considerable extent upon the use of the correct proportions of mordant and dyestuff. If the wool is " overchromed," it will not dye black at all by ordinary processes, as before explained, and it may be accepted that 8 per cent. of bichromate of potash is necessary to produce this effect. Between this amount and the normal 3 or 4 per cent. of mordant there is, however, still a considerable margin, and wool treated with these intermediate quantities may be dyed a good full black, but without doubt the color will be much more sensitive to the action of the light, and fade far more rapidly than if properly mordanted. It may even occur, if the point of overchroming is closely approached, that the color contains within itself, apart from the action of the light or other agent, the elements of self-destruction, because the excess of bichromate beyond what is required to combine with and fix the hæmateïn will gradually oxidize and destroy the color compound.

*Chrome-blacks.*—Additions to mordant-bath when the bichromate mordant is employed.

Many of the following notes are taken from the results of experiments made in the Dyeing Department of the Yorkshire College :—

*Action of mineral acids.*—Sulphuric acid is the only one which is of any practical use, and its action depends largely upon the proportion employed. The use of quantities which satisfy the following equation (equal molecules) results in the liberation of chromic acid, and the wool acquires a yellow color, probably due to the chromium being partially fixed as chromic acid.

$K_2Cr_2O_7 + H_2SO_4 + H_2O = K_2SO_4 + 2H_2CrO_4.$ The molecular weight of $K_2Cr_2O_7$ being 294, while that of $H_2SO_4$ is 98, the above reaction requires (considering the substances as pure) three parts by weight of the former to one of the latter ; or, in other words, if 1 per cent. of sulphuric acid is

added when mordanting with 3 per cent. bichromate, the actual mordant is chromic acid; and since the latter exerts a more energetic oxidizing action than bichromate, the activity of the mordant is thus increased. The result of this is that the dye-stuff is more powerfully acted upon, any hæmatoxylin being changed into hæmateïn, or, in the absence of the former, a corresponding amount of hæmateïn being over-oxidized. Practically, then, the effect of adding sulphuric acid to the bichrome mordant in the above proportion is to increase the depth of shade if fresh logwood is employed, while, if aged wood is used, a darker but duller color is obtained for reasons which have been fully explained previously. Identical results are obtained by mordanting with an equivalent amount of pure chromic acid.

It should be noted that under certain circumstances, such, for instance, as the wool retaining alkali from the scouring bath, it may be necessary to use more than the one-third proportion of acid ; but, ordinarily, any excess tends to prevent the fixation of the mordant, and is therefore injurious.

Wool mordanted with a bichromate, and more especially with chromic acid, is previous to being dyed very readily acted upon by light ; the chromium on the exposed portion being reduced more or less completely, according to the intensity of the light and the duration of the exposure. It is important that dyers should recognize this, because the exposed and un-exposed portions dye up slightly different shades.

*Actions of organic acids and salts.*—It will be convenient to consider first the action of tartaric acid. The initial effect of adding this acid is exactly the same as that produced by sulphuric acid, *i. e.*, liberation of chromic acid, thus—
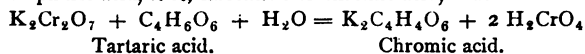
$$K_2Cr_2O_7 + C_4H_6O_6 + H_2O = K_2C_4H_4O_6 + 2\ H_2CrO_4$$
          Tartaric acid.                          Chromic acid.

This reaction requires 1.5 per cent. tartaric acid to 3 per cent. bichrome, and the same effect up to this point can be produced in a very much cheaper manner by using sulphuric acid. On looking at the two equations, however, it will be noticed that in addition to chromic acid there is a second substance pro-duced, *i. e.*, potassium sulphate when sulphuric acid, and potassium tartrate when tartaric acid, is used. The former substance will not react in any way with chromic acid, and

therefore the products are final; but on heating the solution containing chromic acid and neutral potassium tartrate, a further reaction ensues—the chromic acid becoming partially reduced. The reduction is much less, however, than would be the case if the original free tartaric acid were added to the chromic acid instead of to the bichromate, and therefore, to produce the maximum reduction, both the chromic acid and tartaric acid should be in the free state; and it follows from this that, whenever tartaric acid is employed with the bichrome mordant, an amount of sulphuric acid sufficient to liberate the chromic acid should be used along with it.

To effect complete reduction of the bichromate, 3 per cent. of the latter requires about 6 per cent. of tartaric acid; and wool mordanted with these amounts acquires a grayish-green color, owing probably to the deposition of chromic hydrate or basic tartrate. As already explained, this constitutes a non-oxidizing chromium mordant, and thus produces much brighter and more bloomy shades than the yellow or oxidizing mordant obtained with bichrome alone, or with addition of sulphuric acid (compare Patterns 15 and 16, 17 and 18). However, by using sulphuric acid to liberate the chromic acid, it is from that 3 per cent. $K_2Cr_2O_7$ + 1 per cent. sulphuric acid + 4.5 per cent. tartaric acid give almost the same result at considerably less cost (compare Patterns 18 and 19).

In practice cream of tartar (potassium bitartrate) is more commonly used than free tartaric acid; but, if sulphuric acid is added to liberate the tartaric acid (and this should always be done), the action of this substance is, however, exactly the same. Two amounts of sulphuric acid are therefore required in this case, one to liberate the chromic acid from the bichromate of potash, and the other to liberate the tartaric acid from the cream of tartar. It is found by experiment that

3 per cent. $K_2Cr_2O_7$ requires 1 per cent. $H_2SO_4$,

3 " " + 2.5 per cent. tartar, requires 1.5 per cent. $H_2SO_4$,

3 " " + 5 per cent. tartar, requires 2 per cent. $H_2SO_4$,

and the cream of tartar is in this way rendered much more efficacious than if used without addition of sulphuric acid.

If unadulterated, argol is the cheapest form in which to use

potassium bitartrate, and pattern No. 20, which was mordanted with

> 3 per cent. bichromate of potash,
> 5 " argol,
> 2 " sulphuric acid,

is shown as indicating a cheap method of obtaining the green or non-oxidizing mordant.

*Oxalic acid.*—With the exception of tartaric acid and the tartrates, oxalic acid is the most commonly used assistant when a strongly oxidizing mordant is objectionable. Curiously enough, the action of oxalic acid is much less marked than that of tartaric acid. 12 per cent of the former has much less effect than even 4 per cent. of the latter, and under no practicable conditions can the reduction of bichromate of potash be completely brought about in the mordant-bath by means of oxalic acid.

The addition of 2 to 5 per cent. oxalic acid to 3 per cent. bichromate is nevertheless useful in certain cases, notably when mixing logwood with coerulein and some other of the coal-tar dyestuffs. But for a color consisting principally of logwood this assistant is not (with $K_2Cr_2O_7$ mordant) to be recommended.

Many other organic acids, such as citric, malic, succinic, lactic, etc., have been tried experimentally as reducing agents for the bichromate, but none were found to be so effective as tartaric acid. In America, and possibly elsewhere, rotten apples and turnips and other refuse organic matter of an acidulous character has been employed for the purpose, and indeed some practicable reducing agent cheaper than tartaric acid is greatly to be desired.

*Sulphurous acid as a reducing agent.*—Several years ago, students in the Dyeing Department of the Yorkshire College made experiments with a view of reducing the bichrome mordant by adding bisulphite of soda or sulphurous acid to the mordant-bath. These experiments did not lead to any practical result, but a modification of this process has since been proposed which is stated to produce the requisite green mordant in a cheaper manner than by adding tartaric acid or tartar.* It consists in mordanting the wool with bichromate of

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* See Knecht, Journal of the Society of Dyers and Colorists, Dec., 1889.

potash with or without sulphuric acid, and then working in a separate bath containing sulphurous acid.

In all works where a bleaching or stoving house is available the simplest possible plan would be to run the mordanted goods through in the same manner as would be done for bleaching. This would effectively reduce the bichromate, and unless the bleach-house was worked for its legitimate purpose to its fullest capacity, the additional cost would probably be slight.

Two other points require notice before leaving this part of the subject: First, when it is desired to produce the green mordant, whatever the reducing agent employed, it must not be mixed with the bichromate solution for more than a few minutes previous to its use. Otherwise the reduction already commences before the mordanting begins; and experiment shows that any bichromate acted upon previous to its fixation upon the wool is almost entirely wasted. The reduction must either be simultaneous with or more probably subsequent to the fixation. Secondly, green mordanted wool must not be allowed to dry between the mordanting and dyeing operations. If dried, the shade obtained is much inferior, being dull and weak. The explanation is probably that the normal green mordant is chromic hydrate $(Cr_2(OH)_6)$, but which becomes dehydrated on drying, and thus loses affinity for the dyestuff.

Before leaving the subject of chrome mordant, mention may be made of two other forms in which it is sometimes employed, viz., chrome-alum and chromium-fluoride.

Chrome-alum, of which large quantities are obtained as a by-product in the manufacture of artificial alizarin, is sold in the form of large dark-purple crystals or lumps. Its composition is represented by the formula $K_2Cr_2(SO_4)_4$ 24 $H_2O$, and, weight for weight, it contains only about one-third as much chromium as bichromate of potash; and therefore a comparatively large amount has to be used. Being a salt of chromic oxide, it of course yields chromium in the reduced state to the fibre, and thus produces directly the green mordant. Chrome-alum should not, therefore, be compared as a mordant with bichromate of potash, but rather with bichrome and tartaric acid and other green or non-oxidizing mordants. The em-

ployment of chrome-alum is by no means a novelty, but hitherto it has found only a very limited application. When used alone it yields very little chromium to the fibre in a condition suitable for combination with the dyestuff, but a satisfactory amount is fixed, and a good shade obtained, when a large addition of cream of tartar is used. This, however, makes the mordant more expensive than bichrome and tartaric acid; and this necessity for a large amount of tartar probably accounts for the very limited use of chrome-alum as a mordant.

*The best way of applying chrome-alum.*—Experiments made by students in the Dyeing Department of the Yorkshire College, however, show that very much better results are obtained if oxalic acid is used instead of cream of tartar.

It has been found that (for a medium depth of shade) it is best to mordant with 10 to 12 per cent. (1 molecule) chrome alum, which is equivalent to about 3 per cent. bichromate of potash; to this should be added 2.5 to 3 per cent. (2 molecules) oxalic acid, and the mordanting conducted in the usual way. This addition of oxalic acid gives a very much better shade than 9 to 12 per cent. tartar, and is many times cheaper. (Compare Patterns 21 and 22.) The result is quite as good as that obtained by mordanting with bichromate of potash, tartar and sulphuric acid; and the use of chrome-alum applied in this manner may be strongly recommended when a cheap non-oxidizing chromium mordant is required.

*Single-bath chrome-logwood dye.*—Another very important feature of the chrome-alum and oxalic acid mordant is that by its use chrome-logwood blacks may be dyed in a single bath.

When dyeing by this method, use—

> 6 to 8 per cent. chrome-alum,
> 3 to 4    "    "    oxalic acid,
> 0.5 to 1  "    "    chalk,
> Logwood as required.

The amount of chalk given above (the action of which will be explained below) only holds good when very pure water is used; when employing hard water, this must be decreased or omitted. The relative proportions of chrome-alum and oxalic acid here given, must be strictly adhered to, as any variation, even though slight, may spoil the shade.

Although this single-bath process gives a very good result, more logwood will be required for a given shade than would be the case if the mordant were applied first ; but the saving of one process is an equivalent set-off for this loss in material.

Unless the process is carefully conducted, these single-bath shades are liable to be uneven and speckled.

*Chromium-fluoride.* — Chromium - fluoride, or " fluor-chrome," as it is termed, is sold as a rich dark-green crystalline powder, and has the composition $CrF_34H_2O$. Weight for weight, it contains one-fourth less chromium than bichromate of potash, but almost three times as much as chrome-alum. Like the latter, it is, of course, a non-oxidizing mordant, giving at once the green chromic hydrate. It should also be used in the same manner as chrome alum, *i. e.*, with an addition of 2 molecules oxalic acid (see Pattern 23).

*Action of lime-salts in dye-bath.*—In conjunction with chrome mordant, it is very necessary to consider the effect exerted by lime-salts when present in the dye-bath. The great practical importance of this is obvious when we remember that all natural waters contain more or less lime. Briefly stated, the results of experiments which have been made upon this point show that when the yellow mordant is used the effect of a lime-salt in the dye-bath is injurious ; while the opposite is the case with most samples of logwood when using the green mordant. Dyeing experiments with the pure coloring matters have also shown that the shade obtained with hæmatoxylin is much improved by the presence of some lime-salt in the dye-bath if the green mordant is used, but not so with the yellow mordant ; while hæmateïn is better without the lime in either case. This allows the whole of the above results to be explained by the fact that commercial logwood almost always contains both hæmatoxylin and hæmateïn. If the oxidizing (yellow) mordant is used, this itself changes any hæmatoxylin into hæmateïn in the dye-bath ; whereas if the green (non-oxidizing) mordant is employed, some substance must be added to effect the change, or else the hæmatoxylin is wasted ; and calcium carbonate, or more especially acetate, are found useful for this purpose. The lime-salt does not, of course, act directly as an oxidizing agent, but predisposes the

hæmatoxylin to combine with the oxygen in the atmosphere, during the dyeing process.

It is, of course, impossible to give any general rule as to the amount of lime which should be used. There is always a definite amount which will produce the best possible result in each case, and it will vary (first) with the character of the water, and (second) with the amount of hæmatoxylin present in the sample of logwood employed. The amount should, therefore, be determined by each dyer for himself, using his own process, materials, etc.

*Varying the tone of chrome-blacks.*--The principal use of the chrome mordant in conjunction with logwood is for the production of blacks, the normal color produced by this mordant being a blue black. The brilliancy of this may be varied by using the green or yellow mordant, as before explained; but, in order to alter the *tone* of the black, it is necessary to make some further addition either to the mordant-bath or dye-bath. Sometimes a small amount of another mordant, such as aluminium sulphate or copper sulphate, is added to the chrome bath. The effect of the former is to make the shade brighter and more purple, while the latter neutralizes the blue tone, and thus produces a "dead" black. When using mixed mordants, the effects of the "assistants" upon each must be kept in mind, and it is well also to remember the influence exerted upon the "fastness" of the color. For example, an addition of alum will make the color more fugitive, while copper sulphate will have an opposite effect.

More radical changes in the tone of the black may be brought about by additions to the dye-bath. A small amount of some suitable yellow coloring matter, such as fustic or alizarin-yellow, together with a little red (camwood, madder or alizarin), produces a "dead" black, especially if copper sulphate is added to the mordant-bath. A larger proportion of yellow dye alone gives a greenish black, while a red tone is imparted by a slight excess of red dyestuff. If a purplish "bloomy" black is required, a little stannous chloride should be added to the dye-bath five or ten minutes before the end of the dyeing operation. An addition of sumac, or other tannin matter, is also not unusual, but it is much more rationally employed when iron mordant is used.

*Action of milling on chrome-logwood colors.*—In ordinary dyeing processes there is usually, at the end of the operation, a certain small quantity of coloring matter which is absorbed by the wool, but not properly fixed. When the material is subsequently milled, this absorbed dyestuff is removed during the operation, and, if differently colored threads are present, this loose coloring matter will stain and spoil other shades. The colors will "run," or "bleed," as it is expressed. To prevent this occurring in the case of colors which are applied in conjunction with mordants, it is usual to "sadden" with a small amount of mordant after dyeing. To make chrome-logwood colors fast to milling, it is, however, not advisable to use chrome as the saddening agent, although this is frequently done by using about half per cent. bichrome and boiling for five or ten minutes. A better plan for dark shades is to use about 1 per cent. of copper sulphate, since this does not impoverish the color so much. For bright shades 2 per cent. of alum may be substituted.

*Action of light on chrome-logwood colors.*—It is a well-known fact that under the action of the light chrome-logwood colors gradually fade to a grayish green. One explanation of this fact which has been put forward is that the coloring matter gradually fades away—disappears, in fact—and leaves the green chromic oxide exposed to view. A far more reasonable idea has, however, been advanced, according to which the grayish green is simply the color to which the chromium-haematein compound fades. Most colors change as they fade away— many reds to gray, and yellows to brown, and in the same way this color fades to a green.

This "greening" of chrome-logwood colors is their most objectionable feature, and there is no known remedy where light or bright shades are concerned. In the case of blacks, the most satisfactory preventive depends upon the fact that, if some red is added to the grayish-green faded color, the two optically combine and produce a more or less close approximation to black. A small amount of a permanent red coloring matter (nitro-alizarin, for instance) is, to this end, added to the dye-bath, and then as the logwood-color gradually fades, the red becomes more and more prominent, and combining optically in the manner above described tends to maintain the

appearance of black, the fading being thus apparently re-
tarded.

A considerable space has been devoted to the consideration
of the use of chromium mordant in conjunction with logwood,
but not more than is warranted by the interest attached to the
subject. The reason why more attention may well be paid to
this mordant than to any other is twofold. First, it is the
most largely employed, and secondly, there are perhaps more
features of scientific interest connected with its application
than with that of other mordants in general use. Notwith-
standing this, it is by no means true that there is nothing of
importance to be said when speaking of other mordants, and it
is hoped that the following notes will prove of considerable
interest and practical value.

### COPPER MORDANT.

Copper is seldom or never used alone as a mordant for log-
wood, since it does not produce a very pleasing shade. The
only copper salt used in wool-dyeing is the sulphate ($CuSO_4$
$5 H_2O$), commonly known as "blue vitriol" or "bluestone,"
and in conjunction with logwood this mordant gives greenish
grays or blacks with a green tone. When dyeing by the ordi-
nary process ("mordanting and dyeing"), the amount of cop-
per sulphate should vary between 3 and 6 per cent., according
to the amount of logwood used. The assistant which gives the
best result with this mordant is cream of tartar, of which half
the weight of the $CuSO_4$ employed should be used. Binoxa-
late of potash, oxalate of potash or oxalic acid are not good
additions when mordanting with copper sulphate.

Since the copper mordant exerts an oxidizing action upon
the coloring matter, the hæmatoxylin present will be changed
into hæmatein. If, however, a large proportion of unoxidized
coloring matter is present, it may be necessary to add some
lime-salt to the dye-bath, just as is the case with the non-oxi-
dizing or feebly oxidizing chromium mordants. For reasons
stated when previously discussing this point, it is impossible
to give any indication of the amount of lime-salt to use.

In the notes referring to the chromium mordant, it has
already been incidentally mentioned that copper sulphate is the

best mordant to use for the purpose of " saddening " after dyeing, when it is desired to produce the maximum degree of fastness to milling. The true saddening method alone, *i. e.*, applying first the coloring matter and then the mordant, is not satisfactory with copper mordant ; or, in fact, with any other mordant when logwood is the dyestuff. The reason of this appears to be that hæmateïn is so soluble in boiling water, or has so little affinity for the wool fibre, that it does not become fixed in sufficient amount unless the mordant is previously applied.

The " single-bath " method is far more generally used than either the " mordanting and dyeing " or the " saddening " processes. Experiments made upon the effect of adding tartaric and oxalic acids, cream of tartar, and the oxalates of potash, show that in this case as when mordanting with copper sulphate, the tartaric acid compounds give much better results than the oxalates. With 4 per cent. $CuSO_4$, 1 to 1.5 per cent. tartaric acid gives the best result, but if oxalic acid is used 0.5 to 1 per cent. only is required. Excess in either case is very injurious, preventing the fixation of the color-lake upon the wool. In practice, oxalic acid is to be preferred because it is a much better addition than tartaric acid to the iron mordant, in conjunction with which copper sulphate is always used. Such mixtures of logwood extract with copper and iron-salts constitute the " one-dip " or " direct " blacks, and details of the preparation and method of dyeing with these mixtures will be given below.

#### IRON MORDANT.

As a mordant for logwood this metal ranks next in importance to chromium. In point of antiquity the iron mordant easily takes first place, for " copperas blacks " were dyed for a hundred years before the introduction of bichromate of potash as a mordant for wool made " chrome-blacks " possible. The fact that the latter are somewhat easier to dye and are perhaps more reliable, has no doubt been responsible for the preference they usually receive ; but in spite of this the " copperas blacks " are of great interest and importance.

The iron salt almost universally employed as a mordant for logwood is ferrous sulphate ($FeSO_4 7H_2O$), variously known

as " sulphate of iron," " copperas " or "green vitriol." Wool
mordanted with this substance alone acquires a brown color,
owing probably to the deposition of ferric hydrate (or a basic
ferric sulphate) upon the fibre. This does not appear to be a
suitable condition in which to fix the iron upon the wool, since
on dyeing with logwood only a dull bluish-gray shade is pro-
duced. It is evident, therefore, that the same simple process
found suitable when bichromate of potash is the mordant em-
ployed cannot be used with ferrous sulphate. The necessary
modifications of the process take the form of additions to mor-
dant-bath and dye-bath. If, instead of using ferrous sulphate
alone, some cream of tartar is added to the mordant-bath, the
iron is not fixed as a brown ferric salt, but in a colorless
condition—possibly as basic ferrous tartrate—and the dyed
wool has a much darker and brighter color. The proportion
of tartar used should be about 2 molecules to 1 molecule of
ferrous sulphate—say 6 per cent. $FeSO_4$ + 8 per cent. tartar.

Much better results are, however, obtained by using oxalic
acid or binoxalate of potash instead of cream of tartar. With
these assistants not only is the dyed color much fuller and
brighter (see Patterns 24 and 25), but the cost of the mordant
is reduced to a considerable extent. With 6 per cent. $FeSO_4$
use 2.7 per cent. oxalic acid (equal molecules),* or an equiva-
lent quantity of binoxalate of potash. Oxalate of potash is
not a good addition.

The superior result obtained by substituting oxalic acid for
the cream of tartar usually employed, is quite as marked with
ferrous sulphate as with chrome-alum mordant, as will be seen
by referring to the dyed patterns.

Instead of ferrous sulphate, it is possible, with equally good
results, to use *ferric sulphate*, $Fe_4(SO_4)_3$, as mordant. This
salt is sold commercially in an impure state, under the name of
" nitrate of iron," in the form of a dark-brown solution. The
somewhat misleading name no doubt arises from the fact that
nitric acid is used as an oxidizing agent in the manufacture of

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* For further details regarding the respective value of cream of tartar and
oxalic acid as " assistants " to the iron mordant, see " Notes on Mordants
Applicable in Wool-Dyeing."—*Gardner, Journal of the Society of Dyers
and Colorists,* February, 1890.

ferric sulphate ;—to a concentrated solution of ferrous sulphate the necessary amount (a little more than one-third the weight) of sulphuric acid is added, the liquid is then heated to the boil, and nitric acid dropped in until it ceases to blacken the solution. The commercial preparation usually consists of a mixture of ferric sulphate and ferric-nitrate-sulphates. If potassium or ammonium sulphate is added to a solution of ferric sulphate, almost colorless crystals of so-called "iron-alum" are formed. This compound has also been proposed as a mordant for wool, and behaves in a similar manner to ferric sulphate, requiring an addition of oxalic acid.

As a mordant for logwood, ferric sulphate possesses no advantage over the somewhat cheaper ferrous salt, unless it is desired to use a mixture of bichromate of potash and iron mordant, in which case a ferrous salt is inadmissible, since it would be oxidized and precipitated. When used, ferric sulphate should be applied in the same manner as ferrous sulphate, *i. e.*, with addition of oxalic acid, but the amount of the latter should vary according to the composition (acidity, etc.) of the mordant. Ferric sulphate equivalent, in the amount of iron it contains, to 6 to 8 per cent. $FeSO_4$ gives the best result, and the shade obtained is practically identical with that produced by $FeSO_4$ mordant. So, also, is the color produced by mordanting with an equivalent amount of iron-alum (11 to 15 per cent.), but in this case a larger amount of oxalic acid (9 to 10 per cent.) is required; in fact, it is immaterial so far as the shade is concerned, whether ferrous or ferric sulphate, or iron-alum is employed as mordant.

As in the case of chromium and copper mordants, the use of calcareous water in the dyeing operation has a considerable influence when iron is the mordant employed. Whether ferrous or ferric sulphate is used, the presence of a small amount of chalk, and more especially of calcium acetate, adds considerably to the depth and brilliancy of the shade. In this case the principal effect of the lime-salt is to neutralize the acid left in the cloth from the mordanting operation. This may be proved by washing the cloth after mordanting, in a dilute solution of ammonium acetate as well as with water ; by dyeing afterwards with and without chalk the effect of the latter is found to be inappreciable.

With iron mordant applied as indicated above, the color produced on dyeing with logwood is a blue gray or bluish black, similar to the chrome-logwood shade. This may be modified in the same way as the chrome-black, viz., by adding alum or copper sulphate to the mordant-bath; and fustic, madder, etc., to the dye-bath. Tin-salt may also be used for "blooming" the shade, and copper sulphate applied as a "saddening" agent in order to obtain a color fast to milling.

The iron-blacks withstand the action of the light in about the same degree as the chrome-blacks, but, whereas the latter fade to a green, the former yield a gray-colored fade-product. The two classes of blacks may readily be distinguished by spotting a piece of dyed wool with strong sulphuric acid (100° TW), chrome-blacks giving an olive-colored spot, and copperas blacks a red spot.

"*Direct or one-dip*" *blacks.*—These names, amongst others, are given to those preparations containing logwood as dye-stuff, and iron as principal mordant, which are so largely employed for producing blacks by the "single-bath" method.

The possibility of using this method of dyeing depends upon two facts; firstly, that the color-lakes which iron and copper form with hæmateïn, although quite insoluble in water, dissolve unchanged in weak acid solutions; and secondly, that if wool is boiled in this feebly acid solution it will withdraw from the solution and fix upon itself the color-lake; that is to say, the attraction resulting from the affinity between the color-lake and the wool* is able to overcome the tendency of the weak acid to dissolve the color-lake. If, however, the solution is strongly acid, its affinity for, or tendency to dissolve, the color-lake is greater than that of the wool, and therefore no dyeing takes place.

In its simplest form a single-bath black may consist either of hæmateïn-iron lake or the hæmateïn-copper compound. For instance, a blue black may be produced by dyeing with a mixture of:

$$\begin{array}{lll}
30 \text{ to } 40 \text{ per cent.} & & \text{logwood,} \\
4 \text{ `` } 6 & \text{``} & \text{ferrous sulphate,} \\
2 \text{ `` } 3 & \text{``} & \text{oxalic acid.}
\end{array}$$

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* According to Witt's theory, the wool dissolves the color-lake.

Enter the wool into the cold or slightly warm bath, heat gradually to the boil, and boil 30 to 45 minutes (see Pattern No. 28). A green shade of black may also be obtained by using copper sulphate instead of ferrous sulphate :

$$
\begin{array}{rllll}
30 \text{ to } 40 & \text{per cent.} & & \text{logwood,} \\
3 \text{ " } .4 & \text{ " } & & \text{copper sulphate,} \\
0.5 \text{ " } 1 & \text{ " } & & \text{oxalic acid.}
\end{array}
$$

(See pattern No. 26.) It is a singular fact, and one not before noted, that *tartaric* acid gives a much better result than oxalic acid when copper sulphate is employed, while the opposite is the case with the iron-salt. When using a mixture of the two mordants (which is the usual practice), since iron as a rule predominates, it is better to employ oxalic acid.

The patterns annexed also emphasize strongly a fact which will be at once intelligible to the reader. Patterns Nos. 26, 28 and 30 are dyed with an ordinary commercial sample of aged logwood (hæmateïn), Nos. 27, 29 and 31 with an approximately equivalent quantity of logwood extract (hæmatoxylin). It will be noticed that with iron mordant the aged wood gives the best result, while with copper the unoxidized form is much the best. This supports the statement already made, that the ageing of logwood is an oxidation process, since, under the conditions used in dyeing these patterns, the iron mordant does not exert any oxidizing action, while the copper does oxidize the coloring matter.

Ferric sulphate may be substituted for the ferrous salt in dyeing by the above process. It gives a very similar result ; but since no apparent advantage is gained, it is better to use the cheaper ferrous sulphate.

In practice it has not been usual to dye these single-bath blacks in the cheap and simple manner indicated above. Instead of making up the dye-bath when required by adding the various ingredients, the color-lake is previously prepared in bulk by the color-makers and sold to the dyer, either in the form of dry cakes or powders, or water pastes. Many such black preparations are in the market, and they are sold under such names as " one-dip black," " direct black paste,"[1] " nigrosaline," etc. Bousor's black is also a compound of this class. All these are either mechanical mixtures or chemical com-

pounds of logwood extract with copper and iron salts. Some
of the preparations already contain the necessary amount of
acid for their solution, but in most cases the acid has to be
added by the dyer. Other ingredients, such as sumac, fustic
extract, and even acid coal-tar colors, are often present.

Those compounds which are merely mechanical mixtures are
prepared by grinding together to a fine powder the necessary
proportions of solid logwood extract and the iron or copper
salts. In these preparations the color-lake is only produced
when the compound is dissolved, *i. e.*, in the dye-bath.

For the manufacture of those blacks in which the combina-
tion has already taken place, different processes are in vogue.
One method is to heat solid logwood extract until it attains a
liquid condition and then to stir into it the powdered copper
and iron salts. The fluid mass is then allowed to cool and
solidify, and sold either in cake form or ground to powder.
Another process of manufacture is to dissolve the metallic salts
in water and mix with the logwood liquor. The mixture is
then boiled, made alkaline with ammonia or $Na_2CO_3$, which
causes the color-lake to form as a black precipitate, which is
collected and sold as a water paste.

The relative proportions of coloring matter, iron-salt and
copper-salt vary greatly in different preparations, and the charac-
ter and properties of the dyed color will vary accordingly. The
greater the amount of copper in proportion to the iron, the
more permanent will be the color.

Whether prepared as simple mixtures or as chemical com-
pounds, the mode of applying these blacks is the same. If
they already contain the necessary amount of oxalic acid, the
compound is added to the cold or slightly warm dye-bath in
suitable quantity. The wool is then entered, the bath raised
gradually to the boil, and the boiling continued from 30 min-
utes to 1 hour. During the dyeing process the wool gradually
withdraws the color-lake from solution, leaving in the bath the
greater part of the oxalic acid, and as the free acid accumulates
the fixation of the black becomes slower and slower, until a
point is reached at which the solvent power of the acid exactly
counterbalances the attraction of the wool for the color com-
pound, and then, of course, no further dyeing takes place,
however long the material remains in the bath. To overcome

this difficulty, it is usual to add to the bath, as soon as it boils, a small quantity of carbonate of soda (soda crystals), preferably removing the material while the addition is made. The amount of soda added must not be sufficient to bring the bath into an alkaline condition; it should always remain slightly acid. Only the excess of acid must be neutralized, and this may be done, if necessary, once or twice at intervals throughout the process.

When using those preparations which, as sold, contain no oxalic acid, the dyer should proceed exactly as above, after adding the requisite amount of acid. This amount is readily determined by noticing the appearance of the bath, and it is fortunate that there is such a reliable guide, because it is essential for the success of the process that the exact proportion necessary should be used. Before any acid is added, the bath, of course, appears black and muddy, owing to the suspended insoluble color-lake; as the acid is added, this is gradually dissolved, and the liquid assumes a yellow color and is rendered clear. For this effect less acid is required when the bath is boiling than when cold; that is to say, the black precipitate is more soluble in hot than in cold acid solution; and on this account the best plan is to heat the bath (containing half the required amount of water) to the boil, before adding the acid. It is not desirable to entirely dissolve the whole of the black; the fact that a slight turbidity only remains may be taken as an indication that sufficient acid has been used. The bath is then filled up with cold water, and the dyeing conducted in the manner above described.

The preparation of the bath must be attended with great care and exactitude. If an insufficiency of acid is used, the dyed color will, of course, be weak and dull, and, moreover, very liable to rub off, since the black precipitate will be more or less mechanically fixed. On the other hand, an excess of acid prevents the dyeing taking place for reasons already noted; but if, by mistake, any excess has been added, it may be neutralized by carbonate of soda.

Since the different black preparations in the market vary, not only in composition but also in strength, it is impossible to give any precise quantities with which to make up the bath;

but by following the instructions given above, all difficulty will be avoided.

After once using, the bath is by no means exhausted, a certain proportion of the color-lake—which varies according to the acidity of the bath at the end of the operation—remaining in solution. For the second and subsequent lots of material it is therefore not necessary to add as much color as at first, and after each dyeing operation the amount of acid to be added must be determined exactly as in the first instance.

It should be noted that the amount of acid necessary not only varies with the composition and strength of the black, but also depends upon the character of the water ; a calcareous (hard) water requiring for a given quantity of color a larger amount of acid than one containing less lime-salts. The condition of the wool—alkaline from the scourging, or acid from the carbonizing process—will also affect the acidity of the bath, and may therefore have a disturbing influence.

It has already been incidentally mentioned that the shade of these direct blacks may be modified by adding to the bath small quantities of other coloring matters which will dye under similar conditions, *e. g.*, sumac, fustic, or certain of the alizarin or acid coal-tar colors.

*Action of light upon "direct blacks."*—Particular attention should be paid to the following remarks on the action of light upon these single-bath iron and copper blacks. Very serious inconvenience and loss has many times been caused by dyers using these processes without sufficient care in their manipulation, and with inadequate knowledge of the properties of the various ingredients. Every one who attempts to dye with these preparations should be fully cognizant of the fact that he is using a process which, although it gives good results if accurately worked, is extremely sensitive, and any negligence may lead to disastrous consequences.

Under certain conditions, the dyed color possesses the elements of self-destruction, while under certain other conditions it may, after the dyeing process is complete, develop and become darker in color to a remarkable extent. These effects are greatly intensified if the dyed colors are exposed to sunlight. A pure copper-black is a comparatively stable compound, but a pure iron-logwood single-bath color appears to be sensitive

to light, however dyed. Blacks obtained with mixed copper
and iron salts are more or less sensitive, according to which
metal predominates. With regard to the action of oxalic acid,
any excess in the dye-bath, even although the wool is subse-
quently well washed, greatly increases the rapidity of the
fading, some samples changing from black to comparatively
light gray in the course of two or three days. Too little acid
has an opposite effect, the color rapidly developing and chang-
ing (say) from blue to black. It appears probable that the
iron changes readily backwards and forwards from the ferrous
to the ferric state, thus acting as a carrier of oxygen which
either develops or destroys the color according to its condition.
Another interesting fact, first pointed out by Rawson, is that
some other colors (notably soluble blues) are very readily
destroyed by exposure to light when dyed in a bath containing
ferrous sulphate and oxalic acid.

We see, therefore, that a mixture of a single-bath logwood
black with soluble blue, which when dyed possesses a dark-
blue color and forms a good imitation vat indigo-blue, may,
after exposure to light for two or three days, either develop
into a black or fade to a gray, if the slightest mistake is made
in the proportional quantities of ingredients used. And this
one instance will serve to show how extremely cautious dyers
must be in using these direct blacks.

Having now dealt with chromium, iron and copper, which
are the mordants principally used in conjunction with logwood,
it only remains to consider the action of aluminium and tin-
salts. A short note respecting the use of zinc, manganese,
nickel, cobalt, and uranium as mordants is also appended.

### ALUMINIUM MORDANTS.

Before the introduction of the coal-tar colors, logwood-
blues, produced by mordanting with alum, were largely used
as a substitute for indigo-blue. This mordant is still of some
importance in conjunction with logwood, but, like copper, is
generally used as a secondary mordant with the object of
modifying the color. If mixed with bichromate of potash,
for instance, the shade produced by the latter is rendered much
bluer and brighter. Alum cannot, however, be recom-

mended as a good mordant for logwood, in consequence of the colors produced being fugitive to light.

Alum crystals, $\left.\begin{matrix} K_2 \\ Al_2 \end{matrix}\right.$ or $\left.\begin{matrix} K_2 \\ (NH_3)_2 \end{matrix}\right\}$ $(SO_4)_4 24H_2O$, and aluminium sulphate, $Al_2(SO_4)_3$, $18\ H_2O$, are the two forms in which this mordant is used. The latter, sold under the names "lump alum," "cake alum," "rock alum," etc., contains considerably more aluminium than the former, the proportion being 100 to 70. In other words, 10 per cent. aluminium sulphate is equivalent in mordanting power to 14.2 per cent. potash alum, and when used in such equivalent amounts the two salts (if equally pure) give identical results. For a medium shade—say with 10 to 15 per cent. dry logwood—the best amount of aluminium sulphate to use is 6 to 10 per cent., but very poor shades are obtained unless some assistant is used along with the mordant. The two most useful assistants are cream of tartar and oxalic acid; the latter, as will be seen by referring to the dyed patterns (Nos. 32 and 34), producing much more purple shades than the former. If tartar is used, it should be in proportion of four molecules to one molecule of aluminium sulphate, say 10 per cent. $Al_2(SO_4)_3$ $18\ H_2O$ + 11.2 per cent. $KHC_4H_4O_6$. In order to obtain the purple shade, use 6 per cent. $Al_2(SO_4)_3$ $18\ H_2O$ + 5.1 per cent. $(COOH)_2$ (4 molecules). An equivalent amount of binoxalate of potash gives the same result as oxalic acid.

In whatever form the alum mordant is employed, it is absolutely necessary that some lime-salt should be present in the dye-bath. If dyed in pure (distilled) water, only a dull slate-color is produced, whereas an addition of 0.2 to 0.4 gram chalk, or 0.6 to 0.8 gram acetate of lime per litre water, develops a dark-blue or purplish-blue color (compare Patterns 32 and 33). No doubt, most of this simply serves the purpose of neutralizing the acidity which the wool possesses after the mordanting operation, and therefore it follows that the amount of lime-salt which is necessary will be to a great extent influenced by the thoroughness of the washing between mordanting and dyeing. However, even if the mordanted wool is thoroughly neutralized before dyeing, some small addition of calcium-salt is necessary; and probably the logwood-blue is a

triple compound or aluminium-calcium-hæmatëate, analogous to alizarin red (aluminium-calcium-alizarate).

The "single-bath" process yields fairly good results, but entails a waste of dyestuff; that is to say, with an equal amount of dyestuff the "two-bath" method gives considerably the fuller color (compare Patterns 34 and 35, dyed respectively with 10 per cent. logwood, in two baths, and 15 per cent. in single bath). The proportions found to give the best result by the short process are :

> 15 per cent. logwood,
> 4 to 6 " aluminium sulphate,
> 2 " calcium acetate,
> 2.6 to 4 " oxalic acid.

Any excess of oxalic acid must be avoided, since even 6 per cent. entirely prevents the dyeing.

The logwood and aluminium blues are much more fugitive to light than the copper, chromium or iron colors, but withstand milling quite as well, and stoving with sulphurous acid much better.

When using the alum mordant along with chromium, they may either be mixed together in the mordant-bath, or the wool may be mordanted with chrome alone and a small amount of alum added to the dye-bath shortly before the end of the operation, to brighten or "bloom" the color. For this purpose, however, the tin mordant is perhaps preferable.

### TIN MORDANT.

Wool suitably mordanted with stannous chloride ($SnCl_2$ 2 $H_2O$) produces purple shades of blue when dyed with logwood. The color is best obtained by using 4 to 6 per cent. $SnCl_2$ with addition of 8 to 10 per cent. (or more) cream of tartar. A fuller and brighter color is produced with 8 to 10 per cent. $SnCl_2$, but the well-known injurious effect of large amounts of $SnCl_2$ upon the wool fibre renders this quite impracticable. With tin mordant the presence of calcium-salts in the dye-bath is very injurious (compare Patterns 36 and 37). The single-bath process does not give good results, probably on account of the reducing action which the $SnCl_2$ exerts upon the coloring matter.

The tin-logwood color is the most fugitive of all the hæmateïn lakes, and the principal use of this mordant is, as indicated above, to produce a purplish "bloom" upon logwood blacks and blues. For this purpose 1 to 2 per cent. $SnCl_2$ should be added to the dye-bath 10 to 20 minutes before removing the wool. Of course, "bloom" produced in this way is of a fugitive character; and although tin-salts may be preferable for this purpose to aniline violets, which are still more easily destroyed by the action of the light, it would be better to obtain the "bloom" by adding a little galleïn to the dye-bath, the mordant used being bichrome.

Muriate of tin (an acid solution of stannous chloride) or some other form of "tin spirits" is also frequently employed instead of stannous chloride.

*Action of manganese, zinc, and other unusual mordants.*—Some years ago a series of experiments were made upon the action of manganese, nickel, cobalt, zinc, and uranium salts as mordants. The results were given in a paper published in the Journal of the Society of Dyers and Colorists.[*] Anthrea-purpurin was the coloring matter used in most of the dye-trials, and therefore, in some cases, the best quality of mordant assistant, etc., may not have been used in the case of logwood.

Manganese, nickel, and cobalt were employed as sulphates; and since these metals usually behave in a similar manner to iron in chemical reactions, it is somewhat remarkable that they give better results without oxalic acid when used as mordants. The ferrous sulphate mordant, it will be remembered, was very greatly improved by addition of this assistant. From 6 to 10 per cent. of either manganous, nickelous, or cobaltous sulphate produce purplish-brown shades, all these metals behaving in a similar manner (the iron shade is a blue black).

Uranous sulphate, $U(SO_4)_2$ is to be preferred as a mordant to the more common uranyl sulphate, $UO_2SO_4$. From 4 to 6 per cent. $U(SO_4)_2$ with 3 to 4 per cent. cream of tartar produces a bluish gray with logwood. This is similar in character to the alizarin-uranium gray, but duller.

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Sulphate of zinc produces dull-purplish blues.

Samples of wool dyed with these more uncommon mordants were exposed to light along with the others dyed upon the usual mordants. Copper gives considerably faster color than any other mordant; then follow, in order of fastness, the chromium, iron, manganese, nickel, and cobalt colors. Zinc and aluminium give still less permanent colors, while uranium and tin give the most fugitive colors.

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Much of the information contained in this pamphlet is, as before stated, the result of work carried out by students in Professor Hummel's Dyeing Laboratory, Yorkshire College. It may well serve, in fact, as an illustration of the system of instruction carried out in that Institution, since a similar, although not in all cases such an exhaustive, series of experiments are carried with each of the principal coloring matters.

In putting together these notes, which are intended ultimately to form part of a more extended work, it was deemed expedient to treat first of logwood, although others of the natural dyestuffs will in due time be dealt with in a similar manner.

Several points of great interest and importance to dyers in connection with the proper application of logwood under varying circumstances have been passed in review; chief amongst which may be mentioned the experiments relating to the composition of freshly cut and " prepared " logwood, resulting in the remarks relative to the utility of the ageing process. It has also been noted—a most important point to practical men—that the *character*, and, therefore, composition of the mordant should vary with the degree of oxidation of the coloring matter; thus logwood extract requires an entirely different mordant to that used for prepared wood, in order that both may give the best possible result. In this connection also it has been found that the action of lime-salts in the dye-bath is of great importance, hardly less indeed than that of the mordant.

The notes respecting the influence of the character, amount, etc., of the mordant upon the fastness of the dyed color to light, as well as many other details, will also, it is hoped, prove of interest and value to the practical dyer, for whom this pamphlet is specially intended.
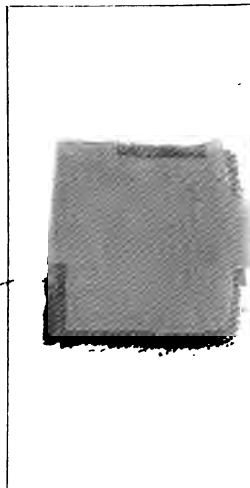
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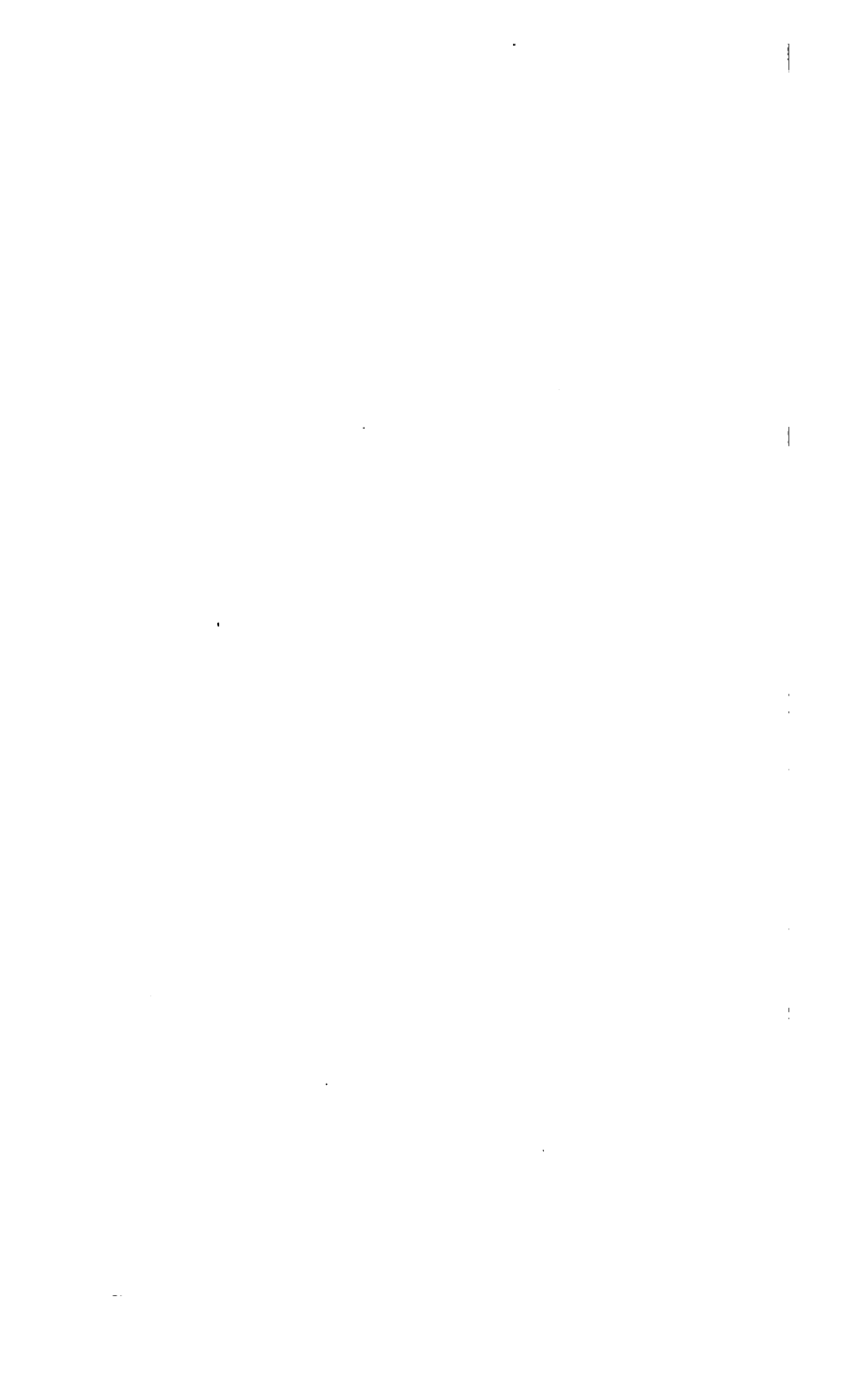
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# LOGWOOD EXTRACT.

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We have the newest and most improved plant and one of the best geographical locations. Our works being situated on the Harbor of New York, and having our own dock, connected with the works and with the rest of our property by rail, we are enabled to get our Logwood direct from the port of shipment without rehandling, or any expense for wharfage, etc.

We are in a position to furnish a Logwood Extract, either solid or liquid, in its highest state of purity, down to any grade that may be called for.

Our Black Dyes for dyeing Cotton and Wool are equal to anything of the kind in the market, and we can give special inducements in prices on these articles.

We should be glad to furnish, through any of our offices, samples of these products, and give quotations.

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### 178 FRONT ST., NEW YORK.

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# PATENTED

# DIAMINE DYES

MANUFACTURED BY

## LEOPOLD CASSELLA & CO.,

### FRANKFORT-ON-MAIN, GERMANY.
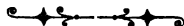
SOLE U. S. AGENTS AND PROPRIETORS OF U. S.
PATENTS:

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## 178 Front St., New York.

# INDIGO EXTRACT,

## CARMINE OF INDIGO

### AND

## INDIGOTINE.

Our works for these products, were erected for the purpose of making them on such a scale as would enable us to enter fully into competition with similar imported articles.

The plant employed is of the newest and most improved type, producing economically the above named articles. Our brands are now well known on the market, and for purity, strength and cheapness they are unequalled.

While we make regularly a certain number of types which have found favor with the consumers, we are always ready to match samples of any quality at the lowest possible price.

Confident that the qualities of our products are of such a character that they could not be excelled, and that our prices are so low as to make us court comparison, quality being considered, with any other makes, whether imported or domestic, we published some years ago detailed methods for testing Indigo Extract, which publication we should be glad to send to anyone interested in the above named product.

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THE

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Fittings and Waste.
Railway, Steamship, Mill and Manufac-
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## GINE, MACHINERY AND
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## SUPERIOR GRADES CYLINDER
## AND VALVE OILS.
## SPECIAL MILL AND MACHINERY
## GREASES.
## WOOL OILS ADAPTED TO SPECIAL
## MANUFACTURES.

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who are using our Oils at their
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### MILLS, ETC.

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*Specifications and Estimates furnished for sup-*
*plying and erecting Pipe Work*
*of every description.*

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**Goods delivered F. O. B. New York.**

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MANUFACTURERS OF

# INDIGO EXTRACTS,
## DYEWOOD AND
### SUMAC EXTRACTS.

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W. C. BARNES & CO., London, England, (Coal Tar Products, Aniline Oils, Salts, etc.)

MANUFACTURE LYONAISE DE MATIERES COLORANTES, Lyons, France, (Makers of Cudbear, Archil Extracts, Artificial Dye Stuffs.)

ALBANY COAL TAR DYE AND CHEMICAL CO., Successors to Albany Aniline Company. (Specialties, Bismark and Acme Browns, Chrysoidines, Indulines, Nigrosines, Reds and Oranges.)

# STANNATE OF SODA.

In 1883, when we took up the manufacture of Stannate of Soda, none of the dealers in this article, and few if any of the manufacturers of it, were willing to guarantee to the consumer the percentage of soluble or available oxide of tin (S. n. o. 2.) it contained. In consequence of this, many of the larger consumers preferred to make it themselves, no matter what the cost, rather than risk using an irregular article, the strength of which no one was in a position to distinctly guarantee.

From the very start, we had analysis made of every lot before offering same for sale, and warranted every package sold to contain the percentage of soluble tin oxide claimed for it.

Our Stannate of Soda is manufactured by a patented process, enabling us to secure the tin used in the compound at no cost whatever, and allowing us to sell the Stannate of Soda at prices below the cost of the materials used by any other process.

We guarantee every pound of Stannate of Soda we sell to contain the percentage of soluble tin oxide claimed for it, and shall be glad to send any users of Stannate of Soda a standard method for testing this product, prepared for us by Dr. P. de P. Ricketts and Dr. Ledoux, with which pamphlet you will be able, whenever you see fit, to verify the guarantee we give as to the strength of our Stannate of Soda.

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